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13. ABSTRACT *(Maximum 200 words)*

Research on non-oxide structure ceramics including silicon nitride, silicon carbide and titanium diboride has been conducted Multiphase silicon nitride composites with melilite and other high nitrogen content grain boundary phases have been prepared. These composites can be sintered to high density and they show improved oxidation resistance. Mechanical properties have been evaluated and found to compare favorably with other silicon nitride materials. Phase relations have alsc been delineated for various rare-earth containing silicon nitride systems. An in-situ toughened alpha silicon nitride solid solution with a microstructure of elongated grains has been discovered. Compared with conventional silicon nitride, this material has a comparable strength and toughness but has 40% higher hardness. Phase relations of selected rare-earth containing alpha silicon nitride solid solutions have also been delineated. Composites of silicon carbide and titanium diboride have been prepared which also show a microstructure of elongated grains. These materials have improved strength and toughness compared to monolithic silicon carbide. In addition, the electrical conductivity has been improved by the addition of titanium diboride.

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I. TITLE OF PROJECT

NON-OXIDE STRUCTURAL CERAMICS - ALLOY DESIGN FOR IMPROVED SINTERABILITY AND MECHANICAL PERFORMANCE

FINAL REPORT

JANUARY 1, 1995 - DECEMBER 31, 1997

U.S. AIR FORCE OFFICE OF SCIENTIFIC RESEARCH
GRANT NO. F49620-95-1-0119

PRINCIPAL INVESTIGATORS:
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II. OBJECTIVES

Alloy design for non-oxide structural ceramics of silicon nitride and silicon carbide is conducted to obtain materials which can be processed by pressureless or low pressure sintering while attaining high toughness and high strength. Sintering aids and transient/equilibrium phase relations will be systematically investigated to understand the densification and microstructure development pathways and to optimize toughening due to grain bridging and duplex microstructures. Micromechanical modeling and mechanical characterization of the developed materials will be conducted to understand the structure-property relations and to develop a comprehensive knowledge base for analyzing performance of structural ceramics under static and cyclic loading conditions over a broad range of temperatures.

III. STATUS OF EFFORT

The effort has been completed and the grant was closed on December 31, 1997. This included a subcontracting portion to the University of Pennsylvania where Professor I-Wei Chen is currently employed. Major accomplishments are summarized below. (a) We have discovered a new form of silicon nitride (in-situ toughened α'-SiAlON) that is of significant industrial interest. This material has a toughness and strength comparable to conventional β-silicon nitride, but is 40% harder, placing it in the same hardness scale as silicon carbide. (b) We have completed a study of silicon nitride with aluminum containing melilite (M'). Methods for sintering and subsequent grain growth treatment have been developed to utilize the nitrogen-rich, refractory M' for transient phase sintering. (c) We have investigated the use of AlN and rare-earth oxides as sintering aids, without aluminum oxides. These ceramics have higher high temperature strength while retaining high toughness at room temperature. (d) We have also completed a study of silicon carbide/titanium diboride composites with elongated 6H/4H SiC. This material has higher strength and toughness than conventional SiC-TiB_2 composites. (e) We have discovered a new mode of crystal growth in the presence of a liquid phase that is particularly relevant for anisotropic grain growth in silicon nitride. The matter is transported from the liquid to the prismatic surfaces of a silicon nitride grain and surface diffusion then takes over to redistribute the matter to the end caps. (f) We have conducted an analytical and micromechanical study of fracture mechanics of fatigue using a grain bridging model. The results are in general accord with the experimental observation of crack growth kinetics and reveal further details concerning the micromechanical origins of fatigue behavior. A further description of these research accomplishments follows.

IV. RESEARCH DESCRIPTION

4.1 In-situ Toughened α'-SiAlON

Rosenflanz and I-W. Chen

Silicon nitride and its related SiAlON solid solutions have two forms: α-Si_3N_4 and β-Si_3N_4. The former is much harder, but only the latter is currently used in engineering applications because only this form can be given a microstructure resembling a whisker-reinforced composite, which gives it the necessary toughness and strength. We have developed methods to reliably synthesize α-SiAlON that has the same whiskery microstructure. As a result, this very hard form of silicon nitride (Hv = 22 GPa) can now be made strong and tough, and is preferred over β-Si_3N_4 for many engineering applications. It should also open up new potential areas in which the ceramic can be applied. The key to the synthesis of whiskery α-SiAlON is to control the nucleation of crystallites and allow them to grow with few impediments in a liquid-wetting fine-grain compact. The nucleation and the growth rates are amenable to manipulation because of nucleation statistics and the strong effect of driving force on kinetics. In silicon nitride, the nucleation statistics can be adjusted by the use of different starting powders which come in either α or β form, while the driving force can be adjusted by the composition of Si, N, Al, O, and various interstitial cations such as rare earth ions (Nd, Gd, Y, Yb, etc.). The physical chemistry of solid and liquid is also an important aspect of the synthesis. Different cation additives alter the acidity/basicity of the liquid affecting the formation of the intermediate phases during sintering. They also have a strong effect on the solubility of α-SiAlON and the viscosity of the liquid. Details of the materials and the methods for preparing them (using α or β Si_3N_4 starting powders, other additives, compositions, firing including hot pressing/gas pressure sintering and annealing) have been disclosed in several patent applications filed by University of Michigan in 1996-1997.

4.2 SiAlON Composites Containing Rare-Earth Melilite and Neighboring Phases

Z-K. Huang, S-Y. Liu, A. Rosenflanz, and I-W. Chen

Sintering aids with a formulation of rare-earth melilite solid solution have been introduced to several SiAlON composites to obtain high density bodies by pressureless sintering and gas pressure sintering. These compositions include ones along the Si_3N_4-R_2O_3:9AlN line, which contains no Al_2O_3 and are known to have excellent strength but very poor sinterability. The structure-property-processing relations are complex and composition dependent. Of most importance is the Al-O content in various phases, which is dictated by the starting composition as well as Al-O solubility in melilite. This influences the sinterability, properties and phase assemblage through the composition of the intermediate liquid and the final β'-SiAlON. La_2O_3 is further used as an effective sintering aid that does not affect the equilibrium phase assemblage. The crystal chemistry and the compatibility of melilite and its neighboring phases have also been investigated and summarized. Lastly, using intermediate, liquid-forming compositions in the $(Y,La)_2O_3$-AlN system as additives, fully dense Si_3N_4 ceramics with high strength at high temperature have been obtained by pressureless sintering with melilite and K' as the grain boundary phases.

4.3 Processing and Properties of SiC-TiB2 Composites

S-Q. Gong and I-W. Chen

The sinterability and microstructure development of SiC-TiB_2 composites using pressureless sintering with oxide additives have been investigated. Dense composites with platelike SiC of a high aspect ratio and a medium grain size were obtained. Compared with conventional SiC, the toughness was higher by 100%. Grains of TiB_2 coarsen in the liquid-rich region preventing the direct coalescence of SiC grains. Frictional pullout of elongated SiC grains was evaluated as the main contributing toughening factor, but its importance is diminished at large grain sizes due to the higher probability of transgranular fracture which could be caused by either oxide segregation or less favorable statistics for intergranular fracture.

4.4 Morphology of Silicon Nitride Grown from a Liquid Phase

L-L. Wang, T-Y. Tien, and I-W. Chen

To explain the recent experimental observation of liquid-grown silicon nitride crystals with a concave depression in the center of the (0001) end face, we propose a new growth mechanism and develop an analytical solution for the steady state. The model allows atoms diffusing via the liquid to the side surface but demands the majority of these atoms be transported to the end caps to feed axial growth. The analysis shows that, for a large radius crystal, the redistribution of atoms by surface diffusion on the end caps requires a long relaxation time, hence a non-equilibrium shape results. For an isolated silicon nitride crystal growing in a liquid environment, the shape of the end cap is largely determined by the ratio of the supersaturation to the equilibrium surface potential, which is inversely proportional to the crystal radius. A large shape distortion is predicted to occur during the growth stage for large radius crystals, and during the coarsening stage for a population of crystals with a large size distribution. This mechanism ceases to operate when the liquid flux to the side surface is blocked, as in silicon nitride ceramics, but is otherwise insensitive to factors such as radial growth kinetics and liquid diffusivities.

4.5 Superplasticity of SiAlON Ceramics

A. Rosenflanz and I-W. Chen

Classical superplasticity of SiAlON ceramics containing Y and Li as additives has been investigated. During deformation, these materials exhibit little microstructural evolution, with negligible growth of elongated β'-phase grains and minimal texture formation. Excellent formabilities are obtained in the temperature range of 1500-1600°C in compression, where a strain of $10^{-2}s^{-1}$ has been achieved, and in punch stretching, where a strain rate of $1.2 \times 10^{-3}s^{-1}$ has been used successfully. Flow stress and fracture stress are both composition dependent allowing for the optimization of formability at a maximum ratio of fracture stress to forming stress at an intermediate lithium composition. Finally, all materials exhibit higher room-temperature bend strength after postforming annealing. Thus, transient superplastic deformation does not impair the ultimate mechanical properties of the materials.

4.6 High Temperature Crack Growth in Silicon Nitride under Static and Cyclic Loading: Short-Crack Behavior and Brittle/Ductile Transition†

S-Y. Liu and I-W. Chen

Crack propagation in Si_3N_4 at elevated temperatures was investigated using controlled surface flaws. Crack growth was generally slower under cyclic than static loading conditions. Concomitantly, there was a tendency for crack growth rate to initially decelerate despite an increasing driving force, exhibiting the so-called short-crack behavior. This tendency became more pronounced at higher temperatures, lower stress intensity factors, and larger cyclic stress variations. A corresponding transition in the crack profile, from a sharp one to a blunt one, was observed. These phenomena are attributed to evolutions of crack-wake shielding. Specifically, with rising temperature and with stress cycling, grain fracture is lowered, triple points are separated, and massive grain pullout is triggered. This mode of pullout mechanism is qualitatively distinct from that operating at lower temperatures, and the transition is believed to occur when the slip length of the grain boundary reaches the average half-length of the grain. This picture is supported by fracture mechanics estimation of crack growth rate, crack opening displacement, and characteristic length of the R-curve based on the pullout mechanism.

† This research was sponsored by the U.S. Air Force under Grant No. AFOSR 91-0094.

4.7 A Model for Fatigue Crack Growth in Grain Bridging Ceramics

I-W. Chen and M. Engineer

A model for fatigue crack propagation based on sliding wear of bridging grains is analyzed for polycrystalline ceramics. Taking into account damage development and crack tip energy balance, we have obtained rigorous solutions for equilibrium and compatibility equations in the crack wake under monotonic and cyclic loading/unloading conditions. Fatigue mechanics in ceramics is found to be formally similar to elastic-plastic mechanics of a path-dependent hardening material, due to the frictional resistance to reverse sliding. It features a load-displacement hysteresis causing energy dissipation and wear, and a longer cohesive zone required for supporting the same peak load with the wear-reduced bridging stresses. The unloading crack opening displacement is strongly dependent on K_{max} and modestly dependent on DK, while the shielding accumulation is strongly dependent on K_{max} and independent of DK. At steady state, when shielding accumulation and shielding degradation are balanced, the fatigue crack growth rate has a form

$$\frac{da}{dN} = A(K_{max})^b(\Delta K)^c$$

where A, b, and c are material-dependent parameters. Fatigue is predicted to have a very high b, a modest c, a higher fatigue resistance for tougher ceramics, and a stronger K_{max} dependence for less tough ceramics. These predictions are in agreement with experimental observations.

V. PERSONNEL SUPPORTED

I-Wei Chen (Principal Investigator)
Zen-Kun Huang (Post-Doc)
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Mehernosh Engineer (Graduate Student)
Shao-qin Gong (Research Student)
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VI. PUBLICATIONS

1. S-Y. Liu and I-W. Chen, "High Temperature Crack Growth in Silicon Nitride under Static and Cyclic Loading: Short-Crack Behavior and Brittle-Ductile Transition," *Acta Metall. Mater.*, **44** [5] 2079-92 (1996).

2. Z-K. Huang and I-W. Chen, "Rare-Earth Melilite Solid Solution and Its Phase Relations with Neighboring Phases," *J. Amer. Ceram. Soc.*, **79** [8] 2091-97(1996).

3. Z-K. Huang, S-Y. Liu, A.. Rosenflanz, and I-W. Chen, "SiAlON Composites Containing Rare-Earth Melilite and Neighboring Phases," *J. Amer. Ceram. Soc.*, **79** [8] 2081-90 (1996).

4. I-W. Chen, S-Y. Liu, and D.S. Jacobs, "Fracture Mechanics of Fatigue of Structural Ceramics," Fracture Mechanics of Ceramics, Vol. 12. Eds. R.C. Bradt, D.P.H. Hasselman, D. Munz, M. Sakai, and V. Ya Shevchenko, Plenum Press, New York, 1996, pp. 1-13.

5. Z-K. Huang, A.. Rosenflanz, and I-W. Chen, "Pressureless Sintering of Si_3N_4 Ceramics using AlN and Rare Earth Oxides," *J. Amer. Ceram. Soc.*, **80** [5] 1256-62 (1997).

6. A.. Rosenflanz and I-W. Chen, "Classical Superplasticity in SiAlON Ceramics," *J. Amer. Ceram. Soc.*, **80** [6] 1341-52 (1997).

7. I-W. Chen and A. Rosenflanz, "A Tough SiAlON Ceramic based on α-Si_3N_4 with a Whisker-like Microstructure," *Nature*, **389**, 701-4, 16 October (1997).

8. L-L. Wang, T-Y. Tien, and I-W. Chen, "Morphology of Silicon Nitride Grown from a Liquid Phase," accepted for publication in *J. Amer. Ceram. Soc.* (1997).

9. I-W. Chen and M. Engineer, "A Model for Fatigue Crack Growth in Grain Bridging Ceramics," under review.

10. S. Gong and I-W. Chen, "Processing and Properties of SiC-TiB_2 Composites," under review.